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**CHROMIUM PLATING AND ELECTROPOLISHING
SOLUTION ANALYSES BY ONLINE X-RAY
FLUORESCENCE SPECTROSCOPY**

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<p>Two increasingly important issues for the chemical processing industry are product quality and productivity. Traditionally, offline chemical analysis has been used to monitor both. The main disadvantage of offline analysis is the loss of time due to sampling, bringing samples to a lab, and waiting for results. Obvious efficiencies can be realized by continuous online chemical monitoring. The initial investment is high, but the return on investment can be very efficient process performance. X-ray fluorescence spectroscopy (online and offline) is investigated and evaluated as a means to quantitatively analyze metal finishing solutions such as actual chromium plating and electroplating solutions for chromium, sulfur, phosphorus, and iron. The identical experiment was conducted at three different manufacturers of this type of instrument, and included calibration, standardization, and analysis. Although this work has a specific objective related to chromium plating and electropolishing liquid samples, much information is related to and provided for other types of samples. Chemical analysis by x-ray fluorescence spectroscopy is nondestructive, applicable to multiple process streams (liquid or solid), and requires no dilutions. In addition, calibration, standardization, and maintenance are minimal. For the specific metal finishing applications discussed, the resultant data do not suggest that this online monitoring technique is useful at this time, but future work may show this technique to be practical.</p>					
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INTRODUCTION

Two increasingly important issues for the chemical processing industry are product quality and productivity. Traditionally, offline chemical analysis has been used to monitor both. The main disadvantage of offline analysis is the loss of time due to sampling, bringing samples to a lab, and waiting for results. Obvious efficiencies can be realized by continuous online chemical monitoring. The initial investment is high, but the return on investment can be very efficient process performance.

Nondestructive x-ray fluorescence spectroscopy is an extremely powerful online and offline technique for the qualitative and quantitative determination of elements above sodium. Many general references on the subject are available (refs 1-8).

Energy dispersive x-ray fluorescence spectroscopy and wavelength dispersive x-ray fluorescence spectroscopy are the two basic types of instrumentation associated with the techniques differing in how x-rays are sorted and measured. Specific background on the former type is abundant (refs 9-15), while the previous general references are useful for the latter type.

Chromium plating and electropolishing solutions are two types of metal finishing solutions that are the specific focus of this work. Offline laboratory methods have been perfected for chemical analyses of these solutions (refs 16-21).

In this work, chemical analysis by online and offline x-ray fluorescence spectroscopy is evaluated for these metal finishing solutions for chromium, sulfur, iron, and phosphorus. In a previous report (ref 22), this author evaluated the use of x-ray fluorescence online analysis of standard reference solution concentrations of chromium plating and electropolishing solutions. Although no past work except by this author has been directed toward this exact application, there has been some related work on trace contaminants and chemical states (refs 23-25).

Excluding this author's work above, Cooper (ref 23) provides perhaps the most information on this general topic. Cooper used a Philips wavelength dispersive x-ray fluorescence spectrometer to determine metal impurities in decorative chromium plating solutions. Sampling was done by a unique method where filter paper was dipped in chromium plating solutions and dried. Sample analysis was done by using the chromium as an "internal standard," since it is kept between specific limits, and comparing its counts to those of a specific metal impurity. The ratio of chromium counts to specific metal impurity count is independent of a sample, can be converted to concentration, and used for comparison.

The most significant impurities, their effects on plating quality, and possible contamination sources are discussed in Cooper's work. These include iron, nickel, copper, zinc, titanium, antimony, lead, tin, aluminum, barium, calcium, and chloride. Detection limits were typically 1 ppm for these elements.

It is significant to note that no attempt was made by Cooper to discuss the determination of other important components in chromium plating solutions (chromic acid, trivalent chromium ion, or sulfate) using this instrument. Cooper's work can be summarized as follows: The filter paper technique appears promising for the determination of sulfate, but increased sensitivity would be achieved by direct solution analysis since sulfur is a low Z element. The determination of chromium by wavelength dispersive x-ray fluorescence spectroscopy presents no difficulties. If the x-ray tube source is used, there is no difficulty in determining sulfate as sulfur. Problems with chromic acid interference can occur if a radioisotope source is used for sulfate determinations.

Additional work in a related area includes using this technique for trace chemical analysis of environmental samples (refs 26, 27).

Both nondestructive online and nondestructive offline x-ray fluorescence spectroscopy are investigated here to determine if these techniques are useful for metal finishing solutions. Although this work has a specific objective related to these liquid samples, much information is related to, and provided for, other types of samples.

THEORY AND BACKGROUND

The analysis of liquids and solids by x-ray fluorescence is a useful, but complex technique. An explanation of this technique is necessary for its evaluation as a chemical analysis technique.

X-rays are part of the electromagnetic spectrum and are capable of ionizing or ejecting electrons from the orbitals of atoms. This ionization is followed by a return to the ground state of the atom and the emission of an x-ray. Atoms of each element emit x-rays with energies that are characteristic of that element, and this is the basis for the analytical use of x-rays.

X-ray fluorescence is a nondestructive spectroscopic method where a sample is irradiated with x-rays, thereby inducing the atoms present in the sample to emit their characteristic elemental x-rays. Detection of these emissions generates analog signals that are converted to digital form for acquisition by a microprocessor. Subsequent processing of the data provides spectral information that identifies the elements and their intensities present in the sample. Concentrations are then calculated from these intensities by fitting the data to stored calibration curves that have been computed from previously analyzed standards.

The principle of x-ray fluorescence involves the atom nucleus and its surrounding electrons' shells (K, L, M, etc.). Electrons in outer shells have greater energy than those in inner shells. When electromagnetic radiation strikes the atom, an inner shell electron may be ejected. To return the atom to its lowest energy state, an outer shell electron will fill the vacancy in the inner shell. Because of this transition, an x-ray will be emitted having an energy equal to the difference between the energy of the electron in its original and final energy states.

Electron shells are identified as K, L, or M progressing outward from the nucleus. Since the energies of these shells are known for all atoms, the x-ray resulting from an electron transition between shells becomes a unique signature of the atom producing it. That is, if the energy of an x-ray can be measured, the element emitting that x-ray can be identified (qualitative analysis). By comparing the number of x-rays emitted by the element per unit time (called x-ray intensity) to the number emitted by a standard, the concentration of that element in a material can be calculated (quantitative analysis) using appropriate assay calculation algorithms (ref 28).

Two basic x-ray fluorescence techniques are available: wavelength dispersive x-ray fluorescence and energy dispersive x-ray fluorescence. The distinction between the two techniques arises from the method by which the x-rays are sorted for measurement.

Using wavelength dispersive x-ray fluorescence, very light elements can be detected from sodium up, for solids and from potassium up, for liquids. In this type of x-ray fluorescence spectrometer, x-rays are directed onto the sample contained in a sample holder or cell, causing excitation of the sample and emission from the sample of secondary x-rays characteristic of the elements contained within the sample. The secondary x-rays are "sorted" in a diffracting crystal and directed onto a detector. There may be a diffracting crystal and separate detector for each element. The x-ray fluorescent spectrometer identifies elements from the angle of the diffracting crystal and the concentration is determined from the count rate or energy of the secondary x-rays. Scanning takes place by rotating the crystal at a known speed and recording the count rate or energy for given angles of diffraction (ref 23).

The wavelength dispersive x-ray fluorescence analyzer is not practical for low Z nonmetallic elements. The heart of the wavelength dispersive x-ray fluorescence analyzer is its up to six-element specific tuned, diffracting crystal spectrometers. The wavelength dispersive x-ray fluorescence detector resolution, which is not given here, is approximately a factor of ten better than an energy dispersive x-ray fluorescence lithium drifted, silicon (Si(Li)) detector (170 eV FWHM at 5.9 keV). The wavelength dispersive x-ray fluorescence crystal spectrometer will provide baseline resolution of adjacent elements, while this is very uncommon for an energy dispersive x-ray fluorescence solid-state Si(Li) detector. By its very nature, the wavelength dispersive x-ray fluorescence analyzer has higher precision, better resolution, faster analysis time, and higher sensitivity than the energy dispersive x-ray fluorescence analyzer.

Energy dispersive x-ray fluorescence is an elemental analysis method that is widely used in industrial laboratory environments. Elements in solids or liquids are nondestructively analyzed in minutes with little or no sample preparation. This capability is further enhanced by the technique's wide dynamic range that allows simultaneous analysis of elements in concentrations from as low as a few parts per million to 100 percent in the same sample. Depending on the analyte concentration, accuracies of less than one percent are attainable with comparable reproducibility (ref 28).

The energy dispersive x-ray fluorescence analyzer is very practical and sensitive for low Z nonmetallic elements. The heart of the energy dispersive x-ray fluorescence analyzer is its solid-state Si(Li) or gas-proportional counter detectors where x-ray emissions are sorted electronically to produce an x-ray spectrum. The energy dispersive x-ray fluorescence detector is compact, sensitive, and flexible for all elements.

Historically, energy dispersive x-ray fluorescence evolved from energy dispersive spectrometry (EDS). In EDS, electron bombardment of the specimen is done by using a scanning electron microscope (SEM) or an electron microprobe instrument. Although the EDS technique associated with SEM is an exceptionally useful method, it should not be considered as a comparable analytical method to energy dispersive x-ray fluorescence. The EDS technique suffers from several disadvantages when it is considered for routine analytical measurements. For example, the specimen must be placed in a high vacuum. It must be conductive or treated with a coating to make its surface conductive. This conductivity is necessary to avoid the problems of specimen-charging associated with charged-particle bombardment. Particle bombardment, especially with electrons, only penetrates the sample surface slightly. Therefore, the resulting x-ray emission fails to represent the bulk composition of the specimen. The sample restrictions, the complicated sample preparation methods, and the expense of the hardware do not meet the requirements of a rapid, simple analytical method that is suitable for use with a variety of materials.

For energy dispersive x-ray fluorescence, an x-ray source is used for sample excitation, thus avoiding charged particle problems from electron bombardment associated with EDS. When x-ray photons of sufficient energy impinge upon an atom, an electron from an inner shell may be photoejected from that atom. The energy required to initiate photoejection is called the absorption-edge energy, and its intensity depends upon the element and the specific electron ejected. The probability of an x-ray photon being absorbed by a sample is represented in x-ray spectroscopy by the mass absorption coefficient. If a plot were made for the mass absorption coefficient versus x-ray energy for copper, then the sudden jump or edge at 8.98 keV would represent the absorption-edge energy required to photoeject a K(1s) electron from copper. An additional increase in the x-ray energy continues to result in the photoejection of K electrons from copper with reduced efficiency. The excess energy is converted into kinetic energy of the photoejected electron (ref 9).

These absorption-edge energies are useful for element filtering techniques. Absorption-edge filters of a certain element are used to filter out higher elements in the same region. For example, titanium filters can be used to filter out or reduce chromium absorption.

If an energy-level diagram for the electrons of copper were made, it could be shown that, after irradiation with x-ray photons of an energy greater than 8.98 keV, some copper atoms in the specimen would have a K-shell vacancy, which is an unstable state. Following spectroscopic selection rules, electrons from outer shells (L and M) would undergo transitions to fill the K-shell vacancy, and, in doing so, they may emit an x-ray photon. The energy of the emitted radiation would be characteristic of the element and of the particular transition. The transitions and their energies for the K lines of copper would be shown in this diagram. Irradiation by lower energy x-radiation will efficiently photoeject electrons from outer shells such as L and M. These processes are important for higher atomic number elements in which the absorption-edge energy for K electrons is very large.

It is important to qualify the statement that x-ray photons may be emitted when a transition occurs, because there is also a competing process taking place. The energy released may be internally converted in the atom to cause the ejection of a secondary, or Auger electron. If this happens, no x-ray photon is emitted.

The fraction of excited atoms that emits x-rays is called the fluorescence yield, which is dependent on the atomic number of the element and the transition involved. A plot of fluorescence yield versus atomic number for K and L emissions shows that they are more difficult to determine by x-ray fluorescence (ref 9). This is due to the low fluorescence yield found in elements of low atomic number and the low energy levels of the x-radiation they emit.

Radiation for sample excitation in online x-ray fluorescence systems is available from both low power (less than 50 watts) and high power primary x-ray radiation from x-ray tubes, x-rays from secondary targets irradiated by x-ray tubes, or x-rays from radioisotope sources. The efficiency of energy dispersive x-ray fluorescence systems allows the use of either low power x-ray tubes or radioactive sources. The most desirable excitation would efficiently excite all the elements, thus providing optimum sensitivity. This is usually not practical due to the great differences in concentration from one element to another and the sometimes great differences in atomic number. To optimize an analysis, the procedure is to analyze a sample over selected energy or elemental ranges by adjusting the excitation parameters.

Of the two sources available for energy dispersive x-ray fluorescence, the x-ray tube is generally the best choice. A radioisotope source is only applicable to a narrow range of elements, its intensity decays in time (half life), and there are additional safety factors to consider. X-ray tubes are flexible, stable, and safe. With the x-ray tube and associated filtering, broad range excitation is provided by one source (ref 28).

The main changes in operating conditions are anode material, tube voltage (where applicable), radioactive source (where applicable), and filters for samples with a wide range of elements. One other consideration is that one percent argon in air may interfere without a helium purge for light element analyses.

Radioisotopic sources are light and inexpensive, while x-ray tube sources are flexible, intense, and have better detection limits. A wide range of elements requires more than one radioisotope source, but only one x-ray tube source (ref 27).

The two types of x-ray detectors used in energy dispersive x-ray fluorescence systems are gas-filled proportional counters and solid-state silicon diodes. Gas-filled detectors are lower in cost, but have somewhat poor spectral resolution. Typically, 10 percent of the energy of the element is analyzed or about 590 eV FWHM for manganese Ka x-rays. Also, gas-filled detectors are generally limited to applications where there are no spectral peak overlaps and the concentrations are above the low ppm range. Silicon detector resolution is considerably better at 200 eV FWHM for manganese Ka x-rays. This performance greatly reduces problems with spectral peak overlaps and enhances sensitivity for trace and lower concentration elements. Some companies have high resolution solid-state detectors, while others have lower resolution gas-filled detectors.

The Si(Li) detector is a layered structure in which a lithium-diffused active region separates the P-type input side from the N-type output side. Under a reverse bias, the active region acts as an insulator with an electric field gradient throughout its volume. When an x-ray photon enters the active region of the detector, photo-ionization occurs and an electron-hole pair is created for each 3.8 eV of photon energy. The electron-hole pairs are swept out of the detector by the applied bias voltage, and the total charge produced in the current pulse is directly proportional to the energy of the x-ray that was absorbed in the detector. The detector and the first stage of the preamplifier are cryogenically cooled by either solid-state thermoelectric or liquid nitrogen cooling to reduce the electronic noise of the device (ref 28).

The x-ray tube/Si(Li) detector has better resolution, precision, and sensitivity than the radioisotope/gas-proportional counter detector (ref 27).

X-ray tube excitation, a solid-state spectrometer, and the IBM PC/AT data processor best use the capabilities of the x-ray fluorescence analysis technique. This combination provides a system that is applicable to a variety of process and elemental analysis applications.

The recently developed x-ray/Peltier thermoelectrically-cooled Si(Li) detector (resolution = 185 eV) is as reliable, but is less bulkier than the x-ray/liquid nitrogen-cooled Si(Li) detector (resolution = 155 eV). The approximately 20 percent degradation has little effect on performance, since resolution for radioisotope/proportional counter detectors is about 1000 eV (ref 27).

These systems can be calibrated with either an empirical analysis method using a group of standards, or with an optional fundamental parameters method that provides analysis with or without standards. Quantitative energy dispersive x-ray fluorescence analysis provides weight percent concentration of the elements.

Many empirical analysis methods are possible. Linear calibration is used if the matrix material is somewhat constant. In these cases, the relationship between the measured intensities and concentrations of the elements is linear. As the concentration increases, the relationship between concentration and intensity becomes nonlinear, and the use of a quadratic curve is more appropriate.

As the composition of a sample becomes more complex, so do the elemental interactions or matrix effects. Corrections for absorption and enhancement effects in the sample are provided through either an intensity or concentration matrix correction.

These systems may be operated with their sensor and processing modules adjacent or remotely configured. The latter is useful if the sensor module must operate in a hazardous environment.

Minimum routine maintenance is required for these systems. The only required periodic maintenance is the replacement of the sample cell windows, spectral calibration, and standardization. Window replacement takes minutes and is done monthly. Where applicable, radioisotope sources must be replaced periodically by the manufacturer.

The special calibration of these systems should be checked daily and can be automated for remote initiation by computer. Standardization is required about every two months (ref 28).

APPROACH

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 29).

Many standard and sample solutions are required. These solutions are prepared (standards) or sampled (samples) to cover the operating ranges of normal production-type chromium plating and electropolishing sample solution analyte concentrations. The six references by Sopok (refs 16-21) provide extensive information for preparing, sampling, and chemically analyzing the standard and sample solutions for all analytes. These six analytical chemistry methods are used for quality control purposes for these solutions.

The general types of analytical systems used are on-stream and off-stream x-ray fluorescence spectrometers that provide elemental (chromium, sulfur, phosphorus, iron) analyses of these solutions. Identical experiments were conducted on this type of instrumentation at Asoma Instruments, Inc., Princeton Gamma-Tech, Inc. (PGT), and Tracor X-Ray, Inc. Each company publishes manuals that are an excellent source of reference for operating conditions and operation and maintenance of these instruments (refs 30-32). Flow streams (online) and grab samples (offline) were analyzed for elements from aluminum through uranium. All solutions were analyzed in triplicate and no dilutions were required.

The experimental approach included calibration and standardization with standard reference chromium plating and electropolishing solutions followed by analysis with sample chromium plating and electropolishing solutions. Calibration and standardization data were used to determine analyte concentrations of sample solutions.

Polypropylene was the most useful window material due to its corrosion resistance to these metal finishing solutions. One mil polypropylene is 50 percent transmitting for sulfur K x-rays.

The acquisition parameters for all nine models are summarized in Table 1. A description of the operating conditions for each instrument used follows.

- Asoma Online Model 8660

The Asoma Online Model 8660 was the most useful instrument from that company for this study.

There are up to 16 sample cells that are designed for liquids and solids at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, window material is polypropylene, and tubing material is Viton™.

The radioisotope excitation source is either Fe-55 (half life 2.7 years), Cm-244 (half life 17.8 years), Cd-109 (half life 1.3 years), or Am-241 (half life 433 years) with a sample aperture and 5-mil beryllium window. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. For optimum excitation, the source radiation must be near in energy to the energy of the x-ray being excited.

The x-ray spectrometer has a gas-filled proportional counter detector with 1000 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.5-mil beryllium window and a pulsed optical feedback preamplifier.

A pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 100 seconds.

The instrument is sold under a general license, and the user is not required to have a license for operation. It meets all U.S. government safety regulations and no radiation badges are required. Radiation safety training is provided at the installation.

- Asoma Offline Laboratory Model EX3000

The Asoma Offline Laboratory Model EX3000 was useful in determining matrix interferences for this study.

The sample tray holds up to ten samples in air, helium, or vacuum environments. Sample types may be solid, powder, liquid, or thin films.

The excitation source is an x-ray tube Bremsstrahlung with a rhodium target anode and a 5-mil beryllium window cooled by natural conduction and convection. The x-ray generator has a 0 to 50 kV range with 0.5 percent stability over 8 hours. Automated fibers include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. Beam collimators are used.

The x-ray spectrometer has a Si(Li) detector with 150 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.3-mil beryllium window, 31-liter liquid nitrogen cooling, and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer in an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 100 seconds.

- Asoma Offline Laboratory Model 8620

The Asoma Offline Laboratory Model 8620 was a low-cost alternative from that company for this study.

There is one sample cell designed for liquids and solids at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, and window material is polypropylene.

The radioisotope excitation source is either Fe-55 (half life 2.7 years), Cm-244 (half life 17.8 years), Cd-109 (half life 1.3 years), or Am-241 (half life 433 years) with a sample aperture and 5-mil beryllium window. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. For optimum excitation, the source radiation must be near in energy to the energy of the x-ray being excited.

The x-ray spectrometer has a gas-filled proportional counter detector with 1000 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.5-mil beryllium window and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 100 seconds.

This instrument is sold under a general license, and the user is not required to have a license for operation. It meets all U.S. government safety regulations and no radiation badges are required. Radiation safety training is provided at the installation.

- PGT Online Courier Model 20

The PGT Online Courier Model 20 was the most useful instrument from that company for this study.

The two multiplexed sample cells are designed for eight liquid or solid streams at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, window material is polypropylene, and tubing material is Viton™.

The radioisotope excitation source is either Fe-55 (half life 2.7 years), Cm-244 (half life 17.8 years), Cd-109 (half life 1.3 years), or Am-241 (half life 433 years) with a sample aperture, 5-mil beryllium window, and 1 to 60 mCi source activity. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. For optimum excitation, the source radiation must be near in energy to the energy of the x-ray being excited.

The x-ray spectrometer has a Si(Li) detector with 195 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.3-mil beryllium window, liquid nitrogen cooling, and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

This instrument is sold under a general license, and the user is not required to have a license for operation. It meets all U.S. government safety regulations and no radiation badges are required. Radiation safety training is provided at the installation.

- PGT Online Wavelength Dispersive Courier Model 30

The PGT Online Wavelength Dispersive Courier Model 30 was a very high resolution instrument for chromium and iron, but was not useful for sulfur and phosphorus. This was the only wavelength dispersive instrument that was studied.

The one multiplexed sample cell is designed for five liquid or solid streams at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, window material is polypropylene, and tubing material is Viton™.

The excitation source is an x-ray tube Bremsstrahlung with a rhodium target anode and a 5-mil beryllium window cooled by tap water. The x-ray generator has a 0 to 50 kV range with 0.5 percent stability over 8 hours.

The x-ray detector uses up to six fixed crystal spectrometers each with its own gas-proportional counter. Each spectrometer is element specific (tuned) with approximately 20 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.5-mil beryllium window and a pulsed optical feedback preamplifier.

The pulse processor is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

This wavelength dispersive x-ray fluorescence system is not useful for elemental analysis below titanium which excludes low Z nonmetallic elements such as phosphorus and sulfur.

- PGT Online Courier Model 10

The PGT Online Courier Model 10 was a low-cost alternative from that company for this study.

There is one sample cell that is designed for liquids and solids at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, window material is polypropylene, and tubing material is Viton™.

The radioisotope excitation source is either Fe-55 (half life 2.7 years), Cm-244 (half life 17.8 years), Cd-109 (half life 1.3 years), or Am-241 (half life 433 years) with a sample aperture, 5-mil beryllium window, and 1 to 60 mCi source activity. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. For optimum excitation, the source radiation must be near in energy to the energy of the x-ray being excited.

The x-ray spectrometer has a gas-filled proportional counter detector with 1000 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.5-mil beryllium window and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

The instrument is sold under a general license, and the user is not required to have a license for operation. It meets all U.S. government safety regulations and no radiation badges are required. Radiation safety training is provided at the installation.

- Tracor Online Spectrace Model 7000/7100

The Tracor Online Spectrace Model 7000/7100 was the most useful instrument from that company for this study.

The eight sample cells are designed for liquids and solids at atmospheric pressure and 0° to 100°C. Sample cell material is Teflon™, window material is polypropylene, and tubing material is Viton™.

The excitation source is an x-ray tube Bremsstrahlung with a silver target anode and a 5-mil beryllium window cooled by natural conduction and convection. The x-ray generator has a 0 to 50 kV range with 0.5 percent stability over 8 hours. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions.

The x-ray spectrometer has a Si(Li) detector with 195 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.5-mil beryllium window, Peltier thermoelectric cooling, and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

- Tracor Offline Laboratory Spectrace Model 5000

The Tracor Offline Laboratory Spectrace Model 5000 was useful in determining matrix interferences for this study.

The sample tray holds up to ten samples in air, helium, or vacuum environments. Sample types may be solid, powder, liquid, or thin films.

The excitation source is an x-ray tube Bremsstrahlung with a silver target anode and a 5-mil beryllium window cooled by natural conduction and convection. The x-ray generator has a 0 to 50 kV range with 0.5 percent stability over 8 hours. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. Beam collimators are used.

The x-ray spectrometer has a Si(Li) detector with 155 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.3-mil beryllium window, 17-liter liquid nitrogen cooling (Peltier thermoelectric cooling optional), and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

- Tracor Offline Laboratory Spectrace Model 6000

The Tracor Offline Laboratory Spectrace Model 6000 was a low-cost alternative from that company for this study.

The sample chamber holds one sample in air, helium, or vacuum environments. Sample types may be solid, powder, liquid, or thin films.

The excitation source is an x-ray tube Bremsstrahlung with a silver target anode and a 5-mil beryllium window cooled by natural conduction and convection. The x-ray generator has a 0 to 50 kV range with 0.5 percent stability over 8 hours. Automated filters include aluminum, copper, cellulose, thick rhodium, thin rhodium, and no filter positions. Beam collimators are used.

The x-ray spectrometer has a Si(Li) detector with 185 eV FWHM resolution for 5.9 keV x-rays at 1000 cps. Other features include a 0.3-mil beryllium window, Peltier thermoelectric cooling, and a pulsed optical feedback preamplifier.

The pulse processor or multichannel analyzer is an analog-to-digital converter whose signal is sent to an IBM PC/AT for analysis, processing, display, and communication. All system operating conditions are also displayed. The analysis time per replicate is 120 seconds.

RESULTS AND DISCUSSION

As mentioned, reagent grade chromium plating and electropolishing solution analyses by online and offline x-ray fluorescence spectrometry were previously investigated by this author (ref 22). It should be noted that online and offline precisions were equal and could be used to monitor the necessary analytes in these reagent-grade metal finishing solutions. This previous experiment assumes very well-known solution concentrations due to the use of reagent-grade chemicals. These precisions were excellent, but this experiment did not address interference problems associated with technical-grade chemicals and the chemical effects of the chromium plating and electropolishing processes.

Experimental data are presented in Tables 2 through 4 for the determination of chromium (as chromic acid and trivalent chromium), sulfur (as sulfuric acid), and iron in five chromium plating sample solutions. Tables 5 through 7 show the same for phosphorus (as phosphoric acid), sulfur (as sulfuric acid), and iron in five electropolishing sample solutions.

Each sample solution has three replicate analyses, a, b, and c. All sample solutions are from actual chromium plating, electropolishing, or combined solutions. Sample solution replicates 4d, 4e, 4f, 9d, 9e, and 9f are from solutions sampled at $130^{\circ} \pm 20^{\circ}\text{F}$ (54°C), while all others are from solutions sampled at $72^{\circ} \pm 10^{\circ}\text{F}$ (22°C). Sample solution temperature does not appear to affect chemical analysis by this method.

Tables 2 through 7 show that, in most cases, the online concentration precisions compare on a range of less than acceptable (chromium, sulfur, and phosphorus) to somewhat acceptable (iron) to Benet's offline precisions. The standard deviation data for these tables is at both the 68 percent confidence level ($1S$ = one sigma or one standard deviation unit) and the 95 percent confidence level ($2S$ = two sigma or two standard deviation units). The 95 percent confidence level is required to control the concentrations of these analytes in their respective metal finishing solutions.

Table 8 presents offline laboratory analyses for trivalent chromium in the five chromium plating sample solutions. The concentration range of this analyte spans the operating ranges of these chromium plating solutions.

Tables 9 and 10 compare worst case two-sigma (95 percent confidence level) precisions of actual chromium plating and electropolishing sample solution analyses by online x-ray fluorescence spectrometry. For PGT, Inc., data in Tables 9 and 10, the first precision value is by energy dispersive x-ray fluorescence, and the second precision value is by wavelength dispersive x-ray fluorescence. All other data are by energy dispersive x-ray fluorescence. Again, it should be noted that online and offline x-ray fluorescence precision data were equal. This experiment assumes fewer well-known solution concentrations due to the use of actual sample solutions that use technical-grade chemicals and have experienced many processing cycles. Analyte concentrations of interest were determined by the best offline laboratory methods available (refs 16-21). The precisions of these experiments by x-ray fluorescence were poorer than the best offline laboratory techniques, but around-the-clock monitoring is the distinct advantage. These poorer precisions are also partly due to interference problems from non-analytes and particulate associated with the analysis of technical-grade chemicals. Calcium and chlorine are two interfering elements that result from tap water and concentrate to levels exceeding five grams per liter.

Table 11 compares worst case two-sigma (95 percent confidence level) precisions of actual chromium plating and electropolishing sample solution analyses by the best offline laboratory techniques available (refs 16-21). It should be noted that the best contractors show poor precisions even after five years of working with them on these techniques.

Table 12 gives an extensive list of online and offline x-ray fluorescence instrument manufacturers. The experiments were conducted at Asoma, PGT, and Tracor because of their superior abilities of analyzing metal finishing solutions by this technique.

For aqueous sample solutions, it was shown that sample cells should sample from a constant head device that will provide a constant positive pressure on the sample cell thin-film windows. The experiment provides chemical analysis of chromium and does not distinguish between trivalent and hexavalent chromium. A recent experiment by this author provides an inexpensive technique to address this problem (ref 22).

This technique is useful for continuous monitoring of aqueous sample solutions such as metal finishing solutions and their associated waste waters. Also, this technique is useful for chemical monitoring of other types of liquid, solid, metallic, or environmental samples. It includes priority pollutants in contaminated soils (ref 27). For aqueous sample solutions, energy dispersive x-ray fluorescence detection limits are about 50 ppm for metallic elements, and about 500 ppm for nonmetallic elements (low Z elements). For solid samples, energy dispersive x-ray fluorescence detection limits are about 1 to 5 ppm for metallic elements, and about 50 ppm for nonmetallic elements (low Z elements). For aqueous sample solutions, wavelength dispersive x-ray fluorescence detection limits are about 10 ppm for metallic elements, and 100 ppm to not practical for nonmetallic elements (low Z elements). For solid samples, wavelength dispersive x-ray fluorescence detection limits are about 0.1 to 1 ppm for metallic elements, and 10 ppm to not practical for nonmetallic elements (low Z elements).

The dip and dry sampling process works for major metal finishing solution analytes, but is not sensitive enough for trace analytes. Since this is an offline analysis method, it was only a minor concern for this work.

Chemical analysis by online x-ray fluorescence is nondestructive, applicable to multiple process streams (liquid or solid), and requires no dilutions. In addition, calibration, standardization, and maintenance are minimal.

Both Tracor and PGT have offered a one-year lease of their most applicable online instruments at a cost of about \$8,000 to further improve precisions on these metal finishing solutions. While the Advanced Technology Branch of Benet Laboratories does not have the man-power resources to further this study, the Physical Science Branch has shown an interest.

This technique is useful for a variety of liquid and solid sample matrices, but generally the precision requirements of the application should be less stringent than these specific metal finishing applications. Although this online analysis technique was successful on reagent-grade reference solutions, it has been unsuccessful to date on actual chromium plating and electropolishing solution samples. For the specific metal finishing applications discussed, the resultant data does not suggest this online monitoring technique is useful at this time; but future work, which will include the investigation of this technique for other metal finishing solutions, metal finishing waste waters, and solid samples, may show this technique to be practical.

REFERENCES

1. E. Bertin, *Introduction to X-Ray Spectrometric Analysis*, Plenum Publishing Corp., NY, 1978.
2. E. Bertin, *Principles and Practice of X-Ray Spectrometric Analysis*, 2nd Edition, Plenum Publishing Corp., NY, 1975.
3. H. Herglotz and L. Birks, *Practical Spectroscopy*, Volume 2, Marcel Dekker, NY, 1978.
4. R. Jenkins, *An Introduction to X-Ray Spectrometry*, Heyden & Son, London, 1974.
5. R. Jenkins, R. Gould, and D. Gedcke, *Quantitative X-Ray Spectrometry*, Marcel Dekker, NY, 1981.
6. R. Tertian and F. Claisse, *Principles of Quantitative X-Ray Fluorescence Analysis*, Heyden & Son, London, 1982.
7. R. Jenkins and J. DeVries, *Practical X-Ray Spectrometry*, Springer-Verlag, Inc., NY, 1967.
8. H. Bauer, G. Christian, and J. O'Reilly, *Instrumental Analysis*, Allyn and Bacon, Inc., Boston, 1989.
9. D. Leyden, "Energy Dispersive X-Ray Spectrometry," *Spectroscopy*, Vol. 2, No. 6, 1987, pp. 28-36.
10. K. Heinrich, D. Newbury, and R. Mykelbust, *Energy Dispersive X-Ray Spectrometry*, Publication 604, NBS, Gaithersburg, MD, 1981.
11. D. Leyden, *Fundamentals of X-Ray Spectrometry as Applied to Energy Dispersive Techniques*, Tracor X-Ray, Inc., Mountain View, CA, 1984.
12. J. Russ, *Fundamentals of Energy Dispersive X-Ray Analysis*, Butterworths, London, 1984.
13. D. Vaughn, *Energy Dispersive X-Ray Microanalysis, An Introduction*, Kevex Corporation, Foster City, CA, 1983.
14. A. Harding, "On-Stream Elemental Analysis by Energy Dispersive X-Ray Fluorescence," *American Laboratory*, Vol. 19, No. 12, 1987, pp. 24-31.
15. S. Little and J. Schindler, "Application of Low Cost Energy Dispersive X-Ray Fluorescence Technology to On-Line Analysis," *Proceedings of the 37th Annual Denver X-Ray Conference*, August 1988.
16. S. Sopok, "Determination of Chromic Acid in Chromium Plating Solutions Using a Redox Titration and Indicator, ARDEC Technical Report ARCCB-TR-89022, Benet Laboratories, Watervliet, NY, August 1989.
17. S. Sopok, "Determination of Sulfuric Acid in Chromium Plating Solutions Using Gravimetric Analysis," Internal Report BITR 91-12, Benet Laboratories, Watervliet, NY, November 1991.
18. S. Sopok, "Utilization of Ion Chromatography and Statistics to Determine Important Acids in Chromium Plating and Electropolishing Solutions," Internal Report BITR 91-10, Benet Laboratories, Watervliet, NY, August 1991.

19. S. Sopok, "Determination of Trivalent Chromium Ions in Chromium Plating Solutions by Ultraviolet-Visible Spectrophotometry," ARDEC Technical Report ARCCB-TR-89030, Benet Laboratories, Watervliet, NY, November 1989.
20. S. Sopok, "Determination of Phosphoric and Sulfuric Acids in Polishing Solutions by Acid-Base Titration Using a pH Meter," ARDEC Technical Report ARCCB-TR-89031, Benet Laboratories, Watervliet, NY, November 1989.
21. S. Sopok, "Determination of Iron in Chromium Plating and Polishing Solutions by Atomic Absorption Spectrometry," ARDEC Technical Report ARCCB-TR-89026, Benet Laboratories, Watervliet, NY, October 1989.
22. S. Sopok, "X-Ray Fluorescence On-Stream Analysis of Standard Reference Solution Concentrations of Chromium Plating and Polishing Solutions," Internal Report BITR 91-3, Benet Laboratories, Watervliet, NY, June 1991.
23. J. Cooper, "Rapid Analysis of Chromium Plating Solutions Using X-Ray Fluorescent Spectrometry," *Transactions of the Institute of Metal Finishing*, Vol. 62, 1985, p. 151.
24. Kawasaki Steel Corporation (Y. Hideko, A. Tadahiro, Y. Noriko, I. Takuji, H. Yoshiichi), "Method and Apparatus for the Determination of Chromium in Chromate Plating Solutions," Japanese Patent Nos. JP8714045A2 and JP6214045, 1987.
25. Y. Gohshi, O. Hirao, and I. Suzuki, "Chemical State Analyses of Sulfur, Chromium, and Tin by High Resolution X-Ray Spectrometry," *Advances in X-Ray Analysis*, Vol. 18, 1975, p. 406.
26. T. Dzubay, *X-Ray Fluorescence Analysis of Environmental Samples*, Ann Arbor Science Publishers, Ann Arbor, MI, 1977.
27. W. Watson, J. Walsh, and B. Glynn, "On-Site X-Ray Fluorescence Spectrometry Mapping of Metal Contaminants in Soils at Superfund Sites," *American Laboratory*, July 1989.
28. *Tracor X-Ray Fluorescence Analyzer Brochure*, Tracor X-Ray, Inc., Mountain View, CA, 1988.
29. J. Fritz and G. Schenk, *Quantitative Analytical Chemistry*, Allyn and Bacon, Inc., Boston, MA, 1987.
30. *Asoma X-Ray Fluorescence Analyzer Operation and Maintenance Manuals*, Asoma Instruments, Inc., Austin, TX, 1988.
31. *PGT X-Ray Fluorescence Analyzer Operation and Maintenance Manuals*, PGT, Inc., Princeton, NJ, 1988.
32. *Tracor X-Ray Fluorescence Analyzer Operation and Maintenance Manuals*, Tracor X-Ray, Inc., Mountain View, CA, 1988.

Table 1. Acquisition Parameters

	Asoma 8660	Asoma EX3000	Asoma 8620	PGT 20	PGT 30	PGT 10	Tracor 7000/7100	Tracor 5000	Tracor 6000
Radioisotope 1	Fe-55 for S & P	NA	Fe-55 for S & P	NA	Fe-55 for S & P	NA	Fe-55 for S & P	NA	NA
Radioisotope 2	Cm-244 for Cr & Fe	NA	Cm-244 for Cr & Fe	NA	Cm-244 for Cr & Fe	NA	Cm-244 for Cr & Fe	NA	NA
Radioactive Activity	100 mCi each	NA	100 mCi each	NA	100 mCi each	NA	100 mCi each	NA	NA
Filter	Varied	Varied	Varied	Varied	Varied	Varied	Varied	Varied	Varied
Lifetime	100 sec	100 sec	100 sec	120 sec	120 sec	120 sec	120 sec	120 sec	120 sec
Max Energy (KeV Range)	Varied	Varied	Varied	Varied	Varied	Varied	Varied	Varied	Varied
Atmosphere	Helium	Helium	Air	Helium	Helium	Helium	Helium	Helium	Helium
Elements	S,P,Cr,Fe	S,P,Cr,Fe	S,P,Cr,Fe	S,P,Cr,Fe	S,P (not useful) Cr,Fe (useful)	S,P,Cr,Fe	S,P,Cr,Fe	S,P,Cr,Fe	S,P,Cr,Fe
Tube Voltage (KV Range)	NA	Varied	NA	NA	Varied	NA	Varied	Varied	Varied
Tube Current (mA Range)	NA	Varied	NA	NA	Varied	NA	Varied	Varied	Varied
Price	\$90,000	\$80,000	\$40,000	\$130,000	\$200,000	\$80,000	\$80,000	\$80,000	\$70,000

Table 2 - Sample Solutions For Chromium As Equivalent Chromic Acid In Chromium Plating Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
0a	239	234	246	244
0b	239	239	248	238
0c	239	229	239	249
1a	262	269	252	257
1b	263	262	255	266
1c	262	267	261	262
2a	244	237	242	250
2b	244	244	247	246
2c	244	235	240	241
3a	250	243	246	261
3b	250	252	252	251
3c	250	251	256	252
4a	254	254	253	255
4b	255	258	247	255
4c	255	258	248	247
4d	---	257	249	257
4e	---	259	255	251
4f	---	252	256	258
Mean				
0	239	234	244	244
1	262	266	256	262
2	244	239	243	246
3	250	249	251	255
4 (a-c only)	255	257	249	252
4 (d-f only)	---	256	253	255
Std Dev (1S)				
0	< 1	4	4	4
1	< 1	3	4	4
2	< 1	4	3	4
3	< 1	4	4	4
4 (a-c only)	< 1	2	3	4
4 (d-f only)	---	3	3	3
worst case (1S)	< 1	4	4	4
worst case (2S)	< 1	8	8	8

Table 3 - Sample Solutions For Sulfur As Equivalent Sulfuric Acid In Chromium Plating Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
0a	2.3	1.8	2.2	2.1
0b	2.4	2.3	2.4	2.0
0c	2.4	1.7	1.7	2.6
1a	2.6	2.9	1.8	2.3
1b	2.6	2.9	2.4	2.5
1c	2.6	2.0	2.6	2.1
2a	2.9	2.6	2.8	2.8
2b	3.0	2.4	2.8	3.1
2c	3.0	3.2	2.2	2.9
3a	2.7	2.7	2.8	2.6
3b	2.7	2.3	2.9	1.9
3c	2.6	2.7	2.5	2.3
4a	3.1	3.1	3.0	3.0
4b	3.1	3.7	2.6	2.6
4c	3.2	2.8	3.2	2.4
4d	---	3.4	2.7	3.4
4e	---	2.9	2.2	3.1
4f	---	3.4	2.9	2.8
Mean				
0	2.4	1.9	2.1	2.2
1	2.6	2.6	2.3	2.3
2	3.0	2.7	2.6	2.9
3	2.7	2.6	2.7	2.3
4 (a-c only)	3.1	3.2	2.9	2.7
4 (d-f only)	---	3.2	2.6	3.1
S. D. (1S)				
0	< 0.1	0.3	0.3	0.3
1	< 0.1	0.4	0.3	0.2
2	< 0.1	0.3	0.3	0.1
3	< 0.1	0.2	0.2	0.3
4 (a-c only)	< 0.1	0.4	0.2	0.3
4 (d-f only)	---	0.2	0.3	0.2
worst case (1S)	< 0.1	0.4	0.3	0.3
worst case (2S)	0.1	0.8	0.6	0.6

Table 4 - Sample Solutions For Iron In Chromium Plating Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
0a	2.1	2.3	2.4	2.7
0b	2.4	2.2	2.7	2.9
0c	1.9	2.6	2.3	2.0
1a	1.1	0.7	0.8	0.9
1b	0.8	0.9	1.1	0.2
1c	1.1	1.2	1.2	1.5
2a	3.5	3.2	3.2	4.1
2b	3.1	3.5	2.9	2.8
2c	3.2	3.5	2.9	4.0
3a	0.6	0.1	0.4	0.7
3b	0.2	0.2	0.3	0.6
3c	0.4	0.6	0.7	1.4
4a	2.9	2.8	3.0	2.0
4b	3.1	2.4	2.7	3.1
4c	2.7	2.7	2.8	3.0
4d	---	3.1	2.8	3.1
4e	---	2.9	2.7	3.4
4f	---	3.0	3.0	2.6
Mean				
0	2.1	2.4	2.5	2.5
1	1.0	0.9	1.0	0.9
2	3.3	3.4	3.0	3.6
3	0.4	0.3	0.5	0.9
4 (a-c only)	2.9	2.6	2.8	2.7
4 (d-f only)	---	3.0	2.8	3.0
Std Dev (1S)				
0	0.2	0.2	0.2	0.4
1	0.1	0.2	0.2	0.5
2	0.2	0.1	0.1	0.6
3	0.2	0.2	0.2	0.4
4 (a-c only)	0.2	0.2	0.1	0.5
4 (d-f only)	---	0.1	0.1	0.3
worst case (1S)	0.2	0.2	0.2	0.5
worst case (2S)	0.4	0.4	0.4	1.0

Table 5 - Sample Solutions For Phosphorus As Equivalent Phosphoric Acid In Electropolishing Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
5a	645	662	660	661
5b	643	672	649	635
5c	646	647	668	649
6a	708	724	699	726
6b	711	691	719	709
6c	704	718	689	726
7a	692	691	684	672
7b	699	674	681	669
7c	699	668	659	692
8a	652	660	665	649
8b	654	686	655	658
8c	650	683	637	633
9a	668	658	664	658
9b	664	689	650	658
9c	665	675	680	672
9d	---	669	657	648
9e	---	685	657	669
9f	---	662	677	655
Mean				
5	645	660	659	648
6	708	711	702	720
7	697	678	675	678
8	652	676	652	647
9 (a-c only)	666	674	665	663
9 (d-f only)	---	672	664	657
Std Dev (1S)				
5	1	10	8	11
6	3	14	12	8
7	3	10	11	10
8	2	12	12	10
9 (a-c only)	2	13	12	7
9 (d-f only)	---	10	9	9
worst case (1S)	3	14	12	11
worst case (2S)	6	28	24	22

Table 6 - Sample Solutions For Sulfur As Equivalent Sulfuric Acid In Electropolishing Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
5a	782	769	794	798
5b	786	783	799	792
5c	782	754	783	785
6a	839	831	862	840
6b	837	856	840	849
6c	845	838	862	862
7a	861	879	854	879
7b	871	868	850	880
7c	870	862	872	898
8a	853	858	855	863
8b	851	867	854	857
8c	856	844	875	874
9a	797	781	829	804
9b	803	781	803	804
9c	794	760	817	788
9d	---	795	821	814
9e	---	791	817	800
9f	---	809	801	814
Mean				
5	783	769	792	792
6	840	842	855	850
7	867	870	859	886
8	853	856	861	865
9 (a-c only)	798	774	816	799
9 (d-f only)	---	798	813	809
Std Dev (1S)				
5	2	12	7	5
6	3	11	10	9
7	4	7	10	9
8	2	9	10	7
9 (a-c only)	4	10	11	8
9 (d-f only)	---	8	9	7
worst case (1S)	4	12	11	9
worst case (2S)	8	24	22	18

Table 7 - Sample Solutions For Iron In Electropolishing Solutions

Sample	Benét (g/l)	Asoma (g/l)	Tracor (g/l)	PGT (g/l)
5a	3.3	3.6	3.4	3.1
5b	3.7	3.8	3.0	2.9
5c	3.6	3.8	3.7	3.5
6a	0.4	0.8	0.2	0.8
6b	0.9	0.9	0.7	1.2
6c	0.3	0.4	0.6	0.9
7a	3.4	3.6	2.6	2.3
7b	2.9	3.0	2.6	3.8
7c	2.7	3.5	3.1	2.9
8a	5.1	5.6	5.7	4.9
8b	5.8	5.7	6.3	5.9
8c	5.8	6.0	5.5	5.7
9a	1.7	2.4	2.4	0.7
9b	1.6	2.8	2.1	1.9
9c	2.2	2.1	2.0	1.2
9d	---	2.0	1.7	1.9
9e	---	2.6	2.5	2.1
9f	---	2.4	1.9	1.6
Mean				
5	3.5	3.7	3.4	3.2
6	0.5	0.7	0.5	1.0
7	3.0	3.4	2.8	3.0
8	5.6	5.8	5.8	5.5
9 (a-c only)	1.8	2.4	2.2	1.3
9 (d-f only)	---	2.3	2.0	1.9
Std Dev (1S)				
5	0.2	0.1	0.3	0.2
6	0.3	0.2	0.2	0.2
7	0.3	0.3	0.2	0.6
8	0.3	0.2	0.3	0.4
9 (a-c only)	0.3	0.3	0.2	0.5
9 (d-f only)	---	0.2	0.3	0.2
worst case (1S)	0.3	0.3	0.3	0.6
worst case (2S)	0.6	0.6	0.6	1.2

Table 8 - Laboratory Analyses For Trivalent Chromium In The Five Sample Solutions

Chromium Plating Sample Solutions	CR(III) (g/l)
0	0.4
1	2.7
2	1.2
3	4.1
4	3.7

Table 9 - Worst Case Two Sigma Precisions Of Chromium Plating Sample Solution Analyses By Online X-Ray Fluorescence Spectrometry

Analyte	Conc Range (g/l)	Asoma Prec (g/l)	Tracor Prec (g/l)	PGT * Prec (g/l)
CrO ₃	240 - 260	8	8	8 / (4.0)
H ₂ SO ₄	2.4 - 3.1	0.8	0.6	0.6 / (NA)
FE	0 - 7.5	0.4	0.4	1.0 / (0.7)

* The first precision value is by energy dispersive x-ray fluorescence, and the second precision value by wavelength dispersive x-ray fluorescence. No data was possible for H₂SO₄ by wavelength dispersive x-ray fluorescence.

Table 10 - Worst Case Two Sigma Precisions Of Electropolishing Sample Solution Analyses By Online X-Ray Fluorescence Spectrometry

Analyte	Conc Range (g/l)	Asoma Prec (g/l)	Tracor Prec (g/l)	PGT * Prec (g/l)
H ₃ PO ₄	640 - 730	28	24	22 / (NA)
H ₂ SO ₄	795 - 895	24	22	18 / (NA)
FE	0 - 15	0.6	0.6	1.2 / (0.7)

* The first precision value is by energy dispersive x-ray fluorescence, and the second precision value by wavelength dispersive x-ray fluorescence. No data was possible for H₃PO₄ or H₂SO₄ by wavelength dispersive x-ray fluorescence.

Table 11 - Worst Case Two Sigma Precisions Of Sample Solution Analyses By The Best Offline Laboratory Methods *

Analyte	Conc Range (g/l)	Benét Prec (g/l)	Best Contractor Prec (g/l)
CrO ₃	240 - 260	0.4	> 3.0
H ₂ SO ₄	2.4 - 3.1	0.1	> 1.0
FE	0 - 7.5	0.4	0.5
H ₃ PO ₄	640 - 730	6	> 20
H ₂ SO ₄	795 - 895	8	> 25
FE	0 - 15	0.6	0.6

* The first three analytes are from sample chromium plating solutions, and the second three analytes are from sample electropolishing solutions.

Table 12. X-Ray Fluorescence Instrument Manufacturers

Alrad Instrument Ltd, England
American Instrument Inc, Reading NJ, 201-636-5770
Applied Research Laboratories, Sunland CA, 818-352-6011
Applied Research Labs, Valencia CA, 805-295-0019
Asoma Instruments Inc, Austin TX, 512-258-6608
Cianflone Scientific Instruments Corp, Pittsburg PA, 412-787-3600
Columbia Scientific Industries Corp, Austin TX, 512-258-5191
Criss Software Inc, Largo MD, 202-249-7522
Dapple Systems, Sunnyvale CA, 408-733-3283
Diano Corp, Woburn MA, 617-935-4310
Dohrmann, Santa Clara CA, 408-727-6000
EDAX International Inc, Mahwah NJ, 201-529-3800
EG&G Instruments Ltd., England
EG&G Ortec, Oak Ridge TN, 615-482-4411
General Electric Co, Cleveland OH, 216-266-2970
Hilger Analytical Ltd., England
Horiba Instrument Inc., Irvine CA, 714-250-4811
International Equipment Trading Ltd, Vernon Hills IL, 312-913-0777
Isotope Products Laboratories, Burbank CA, 818-843-7000
JOEL USA Inc, Peabody MA, 508-535-5900
Jordan Valley Applied Radiation Ltd, Israel
Kawasaki Steel Corp., Japan
Kevex Corp, Foster City CA, 415-573-5866
Leco Corp, St Joseph MA, 616-983-5531
Link Analytical, Redwood City CA, 415-595-5465
LND Inc, Oceanside NY, 516-678-6141
Lumiscope Co. International Ltd, Japan
Machlett Laboratories Inc, Raytheon, Stamford CA, 203-348-7511
Microspec Corp, Fremont CA, 415-656-8820
Molecular Data Corp, Cleveland OH, 216-381-6328
Nuclear Enterprises Ltd, England
The Nucleus Inc, Oakridge TN, 615-482-4041
Outokumpu Electronics, Finland
Ovonic Synthetic Materials Co, Troy MI, 313-362-1290
Oxford Analytical Instruments Ltd, England
Panametrics Inc, Waltham MA, 617-899-2719
Philips Electronic Instruments Co, Mahwah NJ, 201-529-3800
PGT(Princeton Gamma-Tech/Outokumpa), Princeton NJ, 609-924-7310
Questron Corp, Princeton NJ, 609-587-6898
Rayionics Science Inc, Canada
Rigaku/USA Inc, Danvers MA, 508-777-2446
Richard Schoeps KG, West Germany
Scintag Inc, Santa Clara CA, 408-748-8544
Seiko Instruments USA Inc, Torrance CA, 213-517-7700
Shimadzu Scientific Instruments, Braintree MA, 617-849-7777
Siemens Energy & Automation Inc, Cherry Hill NJ, 609-424-9210
Siemens Analytical X-Ray Instruments Inc, Madison WI, 608-273-5019
Somar International Inc, Tuskahoe NY, 914-961-1400
Spectrolab Ltd., England
Spectrum Sciences, Santa Clara CA, 408-727-1567
Sumitomo Metal Industries Ltd., Japan
Tracor X-Ray Inc, Mountain View CA, 415-967-0350
TruFocus Corp, Los Gatos CA, 408-370-1176
Vanslager Assoc Inc, Los Gatos CA, 408-370-7900

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